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(71) Applicant: **Mori, Yasuhiro**
Koto-ku, Tokyo 135-0042 (JP)

(72) Inventors:
- **MORI, Yasuhiro**
  Koto-ku, Tokyo 135-0042 (JP)
- **DETZNER, Peter,**
  ISIMAT GmbH Siebdruckmachinen
  73479 Ellwangen (DE)

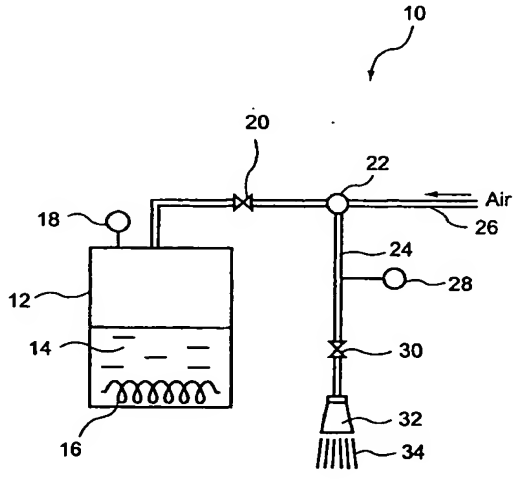
(74) Representative: **Hoffmann, Eckart, Dipl.-Ing.**
Patentanwalt,
Bahnhofstrasse 103
82166 Gräfelfing (DE)

(54) METHOD FOR MODIFYING SURFACE OF SOLID MATERIAL, SURFACE-MODIFIED SOLID MATERIAL AND DEVICE FOR MODIFYING SURFACE OF SOLID MATERIAL

(57) A method for modifying the surface of a solid substrate, a surface modified solid substrate and an apparatus for modifying a surface of a solid substrate which facilitate adhesion, printing, painting and the like are provided.

By providing a method for modifying the surface of a solid substrate, a surface modified solid substrate and an apparatus for modifying a surface of a solid substrate, providing a surface modification apparatus comprising a storage part for storing a fuel gas which comprises a modifying compound which comprises a silicon atom, a titan atom or an aluminum atom, with the respective boiling point being between 10 and 100 °C, a transfer part for transferring said fuel gas to an outlet part, and an outlet part for blow treating with a fuel gas flame, and carrying out blow treatment wholly or partly with a silicatizing flame or the like of the surface of a solid substrate.

Fig. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for modifying a surface of a solid substrate, a surface modified solid substrate and.an apparatus for modifying a surface of a solid substrate, in particular to a method for modifying the surface of a solid substrate, a surface modified solid substrate and an apparatus for modifying a surface of a solid substrate to facilitate adhesion, printing, painting and the like.

BACKGROUND ART

[0002] The surfaces of solid substrates such as silicone rubber, fluorine-contained rubber and polyethylene resin are often hydrophobic and water repellent, making the adhesion of other materials, printing and surface treatment by ultraviolet light painting and the like generally very difficult Metal surfaces such as stainless steel and magnesium on the other hand show the problem of easy paint film detachment in case of directly applying ultraviolet light curing paint and the like, as the adhesive forces and the surface smoothness of the metals among a variety of kinds of metals are insufficient It has further been tried to add inorganic particles such as titanium oxide particles and zirconium oxide particles into the high polymer as a light catalyst, but the distribution properties are poor and the handling is not easy.

[0003] Therefore, as a method of modifying the special surface properties of solid substrates, a primer treatment is applied to the solid substrate surface and/or silane coupling agent and titanium coupling agent solved in a solvent are coated onto the surface.

[0004] However, problems with regard to the manufacturing process emerge such as that a relatively large amount of primer and silane coupling agent and the like and that moreover a long treatment time are required in order to achieve a prescribed modification effect

[0005] Therefore, as a method of modifying the special surface properties of solid substrate in place of the primer treatment and the coupling agent treatment, a ultraviolet light irradiation method, a corona discharge treatment, a plasma treatment, an method for adding a surface functional group, a surface light grafting method, a sandblasting treatment, an acid chromic mixture treatment and the like are exemplified.

[0006] For example, Japanese unexamined published patent application No.1993-068934 discloses a method for improving a wettability and an adhesiveness of a painting by irradiating ultraviolet light onto the surface of the hydrophobic plastics using a high pressure mercury lamp with synthetic quartz glass tube. Further, U.S. patent No. 5098618 discloses a method for improving a wettability and an adhesiveness of a painting by selectively irradiating a ultraviolet light having wavelengths of 185 nm and 254 nm onto the surface of the hydrophobic plastics under a mixed gaseous condition. Further, Japanese unexamined published patent application No.1998-067869 discloses a corona treatment method for spraying a gas onto the surface of the plastics having a poor wettability by applying a high voltage pulse. Further, Japanese unexamined published patent application No.1996-109228 discloses a method for graft polymerization of a vinyl monomer on a surface of a polyolefin and the like after an activation treatment, such as an ozone treatment, a plasma treatment, a corona treatment, a high voltage treatment, an ultraviolet light irradiation method and the like, of the surface of the solid substrate in order to improve a dyestuff-affinity.

[0007] However, these methods for modifying the surface of the solid substrate have a variety of problems, such as environmental problems that working environment is contaminated, dangerous and the like, work-related problems that water washing treatment, waste solution treatment and the like are required, economical problems that large scale and expensive facilities are required in addition to a problem that a modification of the surface of the solid substrate is insufficient

[0008] On the other hand, as a simple and cheap method for modifying the surface of the solid substrate, a flame treatment of the surface of the solid substrate may be suggested. However, according to the method, the modification of the surface of the solid substrate, typically wettability and contact angle characteristics, is insufficient and a problem that the modifying effect of the method cannot last for a long-term exists. Further, as Japanese unexamined published patent application No.1997-124810 discloses, in case of applying the flame treatment onto the surface of the solid substrate, a problem that thermal deformation is easily caused exists.

[0009] Under the circumstances, as German unexamined published patent application No. DE0010019926A1 discloses, the inventors of the present invention propose a method for modifying a surface of a solid substrate mainly such as a metal substrate or a glass article substrate, comprising the steps of: modification of the surface with at least one oxidizing flame; and modification of the surface with at least one silicatizing flame.

[0010] According to the method for modifying the surface of the solid substrate, the surface of the solid substrate may be modified securely and an ink for printing, paint for UV curing and the like may be made to adhere securely.

[0011] However, since the disclosed method for modifying a surface of a solid substrate uses, as a silane compound, alkoxysilane having a high boiling temperature such as tetramethoxysilane (boiling temperature: 122 °C) alone, a

phenomenon that an imperfect combustion may be seen in case of mixing a large quantity of the alkoxysilane compound with air and the like. Further, since the method separately comprises the oxidizing flame treatment, although a superior modifying effect may be obtained, a problem that a treatment time becomes long exists.

[0012] The inventors of the present invention, as a result of their concentrated efforts, have solved the prior art problems by blow treating the surfaces of the solid substrates and metal substrates and the like with a flame from a fuel gas containing modifying compounds having specific boiling points (silicatizing flame treatment, titanium oxidizing flame treatment and aluminum oxidizing flame treatment), have found the features of facilitated combustion, even if a relatively large amount of modifying compound containing silicon atoms and the like is used, and of even and sufficient surface modification of the solid substrate and the like, even if the oxidizing flame treatment process is omitted, and have completed the present invention.

[0013] That is to say, the present invention provides a method for modifying a surface of a solid substrate, a surface modified solid substrate and an apparatus for modifying a surface of a solid substrate respectively, which enable to modify the surface of solid substrates and metal substrates and the like by using the modifying compound burned efficiently and result in a long lasting modification effect

SUMMARY OF THE INVENTION

[0014] According to the present invention, the above-mentioned problems may be solved by providing a method for modifying a surface of a solid substrate wherein the surface of the solid substrate is treated wholly or partly with a flame of a fuel gas which comprises a modifying compound which comprises a silicon atom, a titan atom or an aluminum atom, with the respective boiling point being between 10 and 100 °C.

[0015] That is to say, by limiting the modifying compound boiling points to a prescribed range, the modifying compound evaporates moderately and mixes evenly and rapidly with an inflammable gas such as air and the like and a combustion enhancer, and thereby facilitates perfect combustion. As a result, by using such an evenly mixed fuel gas, the surface modification of the solid substrate easily becomes even and the modification effect easily long-lasting.

[0016] In case of non-suitable modifying compound boiling points and uneven mixing of modifying compound with inflammable gas and the like, due to accumulation of modifying compound or its cross-links or the like not only in the storage part, but also in the tip part of the burner, a problem such as nozzle clogging arises.

[0017] According to the method for modifying a surface of a solid substrate of the present invention, the modifying compound is preferably at least one compound selected from a group consisting of an alkylsilane compound, alkoxysilane compound, alkyltitanium compound, alkoxytitanium compound, alkylaluminum compound and alkoxyaluminum compound.

[0018] By using the above compounds for modifying a surface of a solid substrate, ordinary adhesives as a matter of course, but also inks for printing and UV curing type paints may adhere extremely strongly to the surface of a solid substrate such as silicone rubber, fluorine-contained rubber and the like. Further, by using the above compounds for modifying a surface of a solid substrate, the surface modifying effect cmay last for a longer term.

[0019] According to the method for modifying a surface of a solid substrate of the present invention, at least one compound with a boiling point of 100 °C or above selected from the group consisting of an alkylsilane compound, alkoxysilane compound, alkyltitanium compound, alkoxytitanium compound, alkylaluminum compound and alkoxyaluminum compound is added to the modifying compound in the fuel gas, the added amount preferably having a value in a range from 0.01 to 50 mol% of the total amount of modifying compound.

[0020] By adding a compound with a slightly higher boiling point that is extremely well mutually soluble with modifying compound such as an alkyl silane compound, the problems in handling due to the low boiling point of the modifying compound may be improved and the surface modifying effect of the solid substrate may be significantly increased.

[0021] According to the method for modifying a surface of a solid substrate of the present invention the amount of the modifying compound in the fuel gas preferably has a value in a range from 1×10^{-10} to 10 mol% of the total amount of fuel gas.

[0022] In this way, even if the underground is an electroconductive solid substrate or a colored solid substrate, the surface modifying effect may be achieved in optional places without deterioration of the properties such as electroconductivity and color.

[0023] According to the method for modifying a surface of a solid substrate of the present invention, the modifying compound is preferably heated, evaporated and then burned.

[0024] In this way, even if modifying compounds such as a silane compound are used in a comparably large amount, by mixing the modifying compound evenly into an inflammable gas, the combustion will be enhanced and the modification of a surface of a solid substrate may be carried out evenly and sufficiently.

[0025] According to the method for modifying a surface of a solid substrate of the present invention, fuel gas is preferably obtained by mixing the modifying compound into an air stream.

[0026] In this way, even if modifying compounds such as a silane compound and the like are used in a comparably

large amount, by mixing the modifying compound evenly into the low-priced air stream, the combustion will be enhanced and the modification of a surface of a solid substrate may be carried out evenly and sufficiently.

[0027] According to the method for modifying a surface of a solid substrate of the present invention, the modifying compound is preferably mixed into the air stream by using a carrier gas.

[0028] In this way, even if the modifying compound is difficult to transport due to having a comparably large molecular weight and polar groups, by mixing the carrier gas with the modifying compound evenly into the air stream, the combustion will be enhanced and the modification of a surface of a solid substrate may be carried out evenly and sufficiently.

[0029] According to the method for modifying a surface of a solid substrate of the present invention, the surface of a solid substrate is preferably treated with the flame while the pressure change of the fuel gas is continuously or intermittently monitored.

[0030] In this way, imperfect combustion and the like of the modifying compound may be indirectly prevented and as a result, the modification of a surface of a solid substrate may be carried out evenly and sufficiently.

[0031] According to the method for modifying a surface of a solid substrate of the present invention, the wetting index preferably has a value in a range from 40 to 80 dyn/cm (measuring temperature 25 °C).

[0032] In this way, ordinary adhesives as a matter of course, but also inks for printing or UV curing type paints can adhere extremely strongly. Further, the surface modifying effect may be kept up for a longer time.

[0033] According to the method for modifying a surface of a solid substrate of the present invention, the flame temperature preferably has a value in a range from 500 to 1500 °C.

[0034] In this way, imperfect combustion and the like of the modifying compound may be prevented and ordinary adhesives as a matter of course, but also inks for printing or UV curing type paints may adhere extremely strongly to the solid substrate.

[0035] Further, with such a flame temperature, while the treatment period is also of some influence, a deformation of the solid substrate may be effectively prevented.

[0036] According to the method for modifying a surface of a solid substrate of the present invention, the flame treatment period preferably has a value in a range from 0.1 to 100 seconds.

[0037] In this way, imperfect combustion and the like of the modifying compound may be prevented and ordinary adhesives as a matter of course, but also inks for printing or UV curing type paints can adhere extremely rapidly to the solid substrate.

[0038] Further, with such a treatment period, while the flame temperature is also of some influence, a deformation of the solid substrate may be effectively prevented.

[0039] Another aspect of the present invention is a surface modified solid substrate wherein the surface of the solid substrate is treated wholly or partly with a fuel gas flame so that the wetting index has a value in a range from 40 to 80 dyn/cm (measuring temperature 25 °C), the flame from a fuel gas comprising a modifying compound which comprises a silicon atom, a titanium atom or an aluminum atom, with the respective boiling point being between 10 and 100 °C.

[0040] With this composition, solid substrates or articles obtained thereof may easily be provided wherein ordinary adhesives as a matter of course, but also inks for printing or UV curing (setting) type paints may adhere extremely strongly to the solid substrate. Further, with this composition, the surface modifying effect may be kept up for a longer time.

[0041] According to the composition of the surface modified solid substrate of the present invention, the wetting index of the solid substrate before the surface treatment preferably has a value in a range from 20 to 45 dyn/cm (measuring temperature 25 °C).

[0042] With this composition, solid substrates or articles obtained thereof which optionally have surface-active parts and surface-inactive parts may easily be produced.

[0043] According to the composition of the surface modified solid substrate of the present invention, the solid substrate is at least one inorganic substance selected from the group consisting of aluminum, magnesium, stainless steel, titanium oxide, zinc oxide and zirconium oxide.

[0044] With this composition, inorganic substances may be provided wherein ordinary adhesives as a matter of course, but also inks for printing or UV curing type paints can adhere extremely strongly and inorganic substances may be provided which easily mix and distribute in high-molecular substances.

[0045] According to the composition of the surface modified solid substrate of the present invention, the solid substrate preferably is at least one rubber selected from the group consisting of silicone rubber, fluorine-contained rubber, natural rubber, neoprene rubber, chloroprene rubber, urethane rubber, acryl rubber, olefin rubber, styrene butadiene rubber, acrylonitrile-butadiene, rubber, ethylene-propylene rubber, ethylene-propylenediene rubber, butadiene rubber, butyl rubber, styrene type thermoplastic elastomer and urethane type thermoplastic elastomer.

[0046] With this composition, rubbers or rubber articles obtained thereof may be provided wherein ordinary adhesives as a matter of course, but also inks for printing or UV curing type paints may adhere extremely strongly.

[0047] Further, with such a solid substrate, by appropriate control of the jet condition to assure the flame temperature

has a value in a range from 500 to 1500 °C and the flame treatment period has a value in a range from 0.1 to 100 seconds, a deformation of the solid substrate may be effectively prevented.

[0048] According to the composition of the surface modified solid substrate of the present invention, the solid substrate is at least one resin selected from the group consisting of a polyethylene resin, polypropylene resin, polymethyl pentene resin, polyester resin, polycarbonate resin, polyether sulfone resin, polyacryl resin, polyether ether ketone resin, polyimide resin, polysulfone resin, polystyrene resin, polyamide resin, and polyphenylen sulfide resin, ethylene-tetrafluoroethylen copolymer, polyvinyl fluoride resin, tetrafluoroethylene-perfluoroether copolymer, trafluoroethylene-hexafluoropropylene copolymer, lytetrafluoroethylene resin, lyvinylidene fluoride resin, lytrifluorochloroethylene resin and ethylene-trifluorochloroethylene copolymer.

[0049] With this composition, resin or resin articles obtained thereof may be provided wherein ordinary adhesives as a matter of course, but also inks for printing or UV curing (setting) type paints may adhere extremely strongly.

[0050] Further, with such a solid substrate, by appropriate control of the jet condition to assure the flame temperature has a value in a range from 500 to 1500 °C and the flame treatment period has a value in a range from 0.1 to 100 seconds, a deformation of the solid substrate may be effectively prevented.

[0051] According to the composition of the surface modified solid substrate of the present invention, the solid substrate preferably is at least one thermosetting resin selected from the group consisting of an epoxy resin, phenol resin, cyanate resin, urea resin and guanamine resin.

[0052] With this composition, heat resistant resin or heat resistant articles obtained thereof may be provided wherein ordinary adhesives as a matter of course, but also inks for printing or UV curing (setting) type paints can adhere extremely strongly.

[0053] Further, with such a heat resistant solid substrate, even by wide control of the jet condition to assure the flame temperature has a value in a range from 500 to 1500 °C and the flame treatment period has a value in a range from 0.1 to 100 seconds, a deformation of the solid substrate may be effectively prevented.

[0054] Another aspect of the present invention is an apparatus for modifying a surface of a solid substrate, comprising: a storage part for storing the fuel gas which comprises a modifying compound which comprises a silicon atom, a titanium atom or an aluminum atom, with the respective boiling point being between 10 and 100 °C; a transfer part for transferring the fuel gas to an outlet part; and an outlet part for letting out the fuel gas flame for blow treatment

[0055] With this composition, solid substrates or articles obtained thereof can easily be produced wherein ordinary adhesives as a matter of course, but also inks for printing or UV curing type paints can adhere extremely strongly.

[0056] According to the composition of the apparatus for modifying a surface of a solid substrate of the present invention, a heat supply means in the storage part for producing the fuel gas by evaporating the modifying compound is provided preferably.

[0057] With this composition, a wide range of modifying compounds may be used even in case of a certain distribution of boiling points and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

[0058]

Figure 1 illustrates the structure of a surface modification apparatus of the present invention.
Figure 2 illustrates the blow treatment process by flame with a surface modification apparatus of the present invention.
Figure 3 illustrates the structure of a portable surface modification apparatus of the present invention.
Figures 4 and 5 illustrate the flame blow treatment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0059] Below, with reference to the figures, embodiments regarding the method for modifying a surface of a solid substrate, the surface modified solid substrate and the apparatus for modifying a surface of a solid substrate of the present invention will be explained in detail.

[First Embodiment]

[0060] The first embodiment is a method for modifying a surface of a solid substrate wherein the surface of the solid substrate is blow treated wholly or partly with a flame from a fuel gas, which comprises a modifying compound, with the boiling point being between 10 and 100 °C.

1. Solid Substrate

[0061] According to the first embodiment, the solid substrate used is typically silicone rubber or fluorine-contained rubber or the like. Details will be explained according to the second embodiment.

2. Fuel Gas

(1) Modifying compound

i) Boiling Point

[0062] It is characteristic for the value of the boiling point of the modifying compound under atmospheric pressure to be in a range between 10 and 100 °C.

[0063] The reason for this is, that if the value of the boiling point of the modifying compound is below 10 °C the volatility is extreme and the handling becomes difficult in some cases. On the other hand, if the value of the boiling point of the modifying compound is above 100 °C, the mixing characteristics with inflammable gases and combustion enhancers like air decrease considerably, the modifying compound will tend to imperfect combustion, the surface modification of the solid substrate will be uneven and it will be difficult to keep up the modification effect for a long time.

[0064] Therefore, the value of the boiling point of the modifying compound is preferably in a range between 15 and 80 °C, and even more preferably in a range between 20 and 60 °C.

[0065] The boiling point of the modifying compound may be adjusted not only by restricting the structure of the modifying compound itself, but also by using an appropriate mixture of compounds with comparatively low boiling points like alkyl silane compounds and compounds with comparatively high boiling points like alkoxysilane compounds.

ii) Kinds

[0066] With respect to the kinds of modifying compounds, without any intention of restriction, compounds such as an alkylsilane compound, alkoxysilane compound, alkyltitanium compound, alkoxytitanium compound, alkylaluminum compound and alkoxyaluminum compound may be given as an example.

[0067] Furthermore, among these compounds, an alkylsilane compound, alkyltitanium compound and alkylaluminum compound are preferable modifying compounds as they generally have low boiling points for the most part, are easily evaporated by heating and may be mixed evenly with air and the like.

[0068] As preferable examples of such an alkylsilane compound, alkyltitanium compound and alkylaluminum compound may be given one kind or a combination of two or more kinds of the following: tetramethylsilane, tetramethyltitanium, tetramethytatuminum, tetraethylsilane, tetraethyltitanium, tetraethylaluminum, 1,2-dichlorotetramethylsilane, 1,2-dichlorotetramethyltitanium, 1,2-dichlorotetramethylaluminum, 1,2-diphenyltetramethylsilane, 1,2-diphenyltetramethyltitanium, 1,2-diphenyltetramethylaluminum, 1,2-dichlorotetraethylsilane, 1,2-dichlorotetraethyltitanium, 1,2-dichlorotetraethylaluminum, 1,2-diphenyltetraethylsilane, 1,2-diphenyltetraethyltitanium, 1,2-diphenyltetraethylaluminum, 1,2,3-trichlorotetramethylsilane, 1,2,3-trichlorotetramethyltitanium, 1,2,3-trichlorotetramethylaluminum, 1,2,3-triphenyltetramethylsilane, 1,2,3-triphenyltetramethyltitanium, 1,2,3-triphenyltetramethylaluminum, dimethyldiethyltetrasilane, dimethyldiethyltetratitanium, dimethyldiethyltetraaluminum and the like.

[0069] Furthermore, among such alkyl an silane compound, alkyl titanium compound and alkyl aluminum compound, tetramethyl silane, tetramethyl titanium, tetramethyl aluminum, tetraethyl silane, tetraethyl titanium and tetraethyl aluminum are preferable modifying compounds for their particularly low boiling point and easy mixing characteristics with air and the like, whereas a silane halide compound such as 1,2-dichlorotetramethylsilane are preferable modifying compounds for their particularly excellent surface modifying effect.

[0070] Furthermore, among the above a mentioned compound, alkoxysilane compound, alkoxytitanium compound and alkoxyaluminum compound are preferable modifying compounds as long as their boiling point is in a range between 10 and 100 °C, for although generally having high boiling points in most part due to their ester structure, they enable an even more excellent surface modifying effect of the solid substrate.

iii) Average Molecular Weight

[0071] It is preferable for the value of the weight mean molecular weight (average molecular weight) of the modifying compound to be within a range of 50 to 1,000 measured by mass spectrum analysis.

[0072] The reason for this is, that if the value of the average molecular weight of the modifying compound is below 50 the volatility is high and the handling becomes difficult in some cases. On the other hand, if the value of the average molecular weight of the modifying compound is above 1,000, the evaporation by heating and the easy mixing with air

and the like becomes difficult in some cases.

[0073] Therefore, it is more preferable for the value of the average molecular weight of the modifying compound to be within a range of 60 to 500, and it is even more preferable for the value of the average molecular weight of the modifying compound to be within a range of 70 to 200, measured by mass spectrum analysis.

iv) Density

[0074] It is preferable for the value of the density of the modifying compound in liquid state to be within a range of 0.3 to 0.9 g/cm^3.

[0075] The reason for this is, that if the value of the density of the modifying compound in liquid state is below 0.3 g/cm^3 the handling becomes difficult and accommodation in aerosol cans becomes a problem in some cases. On the other hand, if the value of the density of the modifying compound in liquid state is above 0.9 g/cm^3, the evaporation becomes difficult and in case of accommodation in aerosol cans, a state of complete separation with the air or the like can occur in some cases.

[0076] Therefore, it is more preferable for the value of the density of the modifying compound in liquid state to be within a range of 0.4 to 0.8 g/cm^3, and it is even more preferable for the value of the density of the modifying compound in liquid state to be within a range of 0.5 to 0.7 g/cm^3.

v) Added Amount

[0077] It is preferable for the value of the added amount of the modifying compound to be within a range of 1 x 10^{-10} to 10 mol% of the total amount of fuel gas.

[0078] The reason for this is, that if the value of the density of the modifying compound in liquid state is below 1 x 10^{-10} mol% the modifying effect of solid substrates does not appear in some cases. On the other hand, if the value of the density of the modifying compound in liquid state is above 10 mol%, the mixing properties of the modifying compound with air decrease leading to imperfect combustion of the modifying compound in some cases.

[0079] Therefore, it is more preferable for the value of the density of the modifying compound in liquid state to be within a range of 1 x 10^{-9} to 5 mol%, and it is even more preferable for the value of the density of the modifying compound in liquid state to be within a range of 1 x 10^{-8} to 1 mol%.

(2) Inflammable Gas

[0080] It is preferable to add an inflammable gas into the fuel gas to allow easy control of the flame temperature. Hydrocarbon gases such as propane gas and natural gas, or inflammable gases such as hydrogen, oxygen, air and the like may be given as such inflammable gases. In case of using inflammable gas accommodated in aerosol cans it is preferable to use propane gas and compressed air and the like.

[0081] It is preferable for the value of the contained amount of inflammable gas to be within a range of 80 to 99.9 mol% of the total amount of fuel gas.

[0082] The reason for this is, that if the value of the contained amount of inflammable gas is below 80 mol% the mixing properties of the modifying compound and air decrease leading to imperfect combustion of the modifying compound in some cases. On the other hand, if the value of the contained amount of inflammable gas is above 99.9 mol% the modifying effect of solid substrates does not appear in some cases.

[0083] Therefore, it is more preferable for the value of the contained amount of inflammable gas to be within a range of 85 to 99 mol%, and it is even more preferable for the value of the contained amount of inflammable gas to be within a range of 90 to 99 mol%.

(3) Carrier Gas

[0084] It is preferable to also add a carrier gas to evenly mix the modifying compound into the fuel gas. That is to say, it is preferable to premix the modifying compound with a carrier gas, and to then mix it into the inflammable gas such as the air stream.

[0085] The reason for this is, that by adding a carrier gas, even when using a modifying compound with a relatively high molecular weight that is difficult to transport, it may be evenly mixed into the air stream. That is to say, by adding a carrier gas, the modifying compound becomes easy to burn and the surface modification of the solid substrate may be carried out evenly and sufficiently.

[0086] As such a preferable carrier gas it is preferable to use the same type of gas as the inflammable gas, for example, air and oxygen, or hydrocarbon gases such as propane gas and natural gas may be given.

(4) Additives

i) Kinds

[0087] It is preferable to add at least one compound selected from the group consisting of an alkylsilane compound, alkoxysilane compound, alkyltitanium compound, alkoxytitanium compound, alkylaluminum compound and alkoxyaluminum compound with a boiling point of 100 °C or above into the fuel gas as a modification enhancer.

[0088] The reason for this is, that by adding a modification enhancer with excellent mutual solubility to the modifying compound such as alkyl compound and the like, even when using a compound with a relatively high boiling point, due to the boiling point of the modifying compound being low, the fuel gas handling may be improved and as a consequence thereof the surface modification effect of the solid substrate may be further increased.

ii) Added Amount

[0089] It is preferable for the value of the added amount of modification enhancer to be within a range of 0.01 to 50 mol% of the total amount of modifying compound.

[0090] The reason for this is, that if the value of the added amount of modification enhancer is below 0.01 mol% the effect of adding modification enhancer will not appear in some cases. On the other hand, if the value of the added amount of modification enhancer is above 50 mol% imperfect combustion of the fuel gas occurs in some cases.

[0091] Therefore, it is more preferable for the value of the modification enhancer to be within a range of 0.1 to 30 mol%, and it is even more preferable for the value of the modification enhancer to be within a range of 0.5 to 20 mol%.

3. Flame

(1) Temperature

[0092] It is preferable for the value of the flame temperature to be within a range of 500 to 1,500 °C.

[0093] The reason for this is, that if the value of the flame temperature is below 500 °C, it becomes difficult to prevent effectively imperfect combustion of the modifying compound in some cases. On the other hand, if the value of the flame temperature is above 1,500 °C, the solid substrate subject to surface modifying will be deformed or damaged in some cases, and the types of solid substrates that may be used will be excessively limited in some cases.

[0094] Therefore, it is more preferable for the value of the flame temperature to be within a range of 550 to 1200 °C, and it is even more preferable for the value of the flame temperature to be within a range of 600 to 900 °C.

[0095] The flame temperature may be appropriately adjusted according to the type of fuel gas, the fuel gas throughput or the type and amount of modifying compound added to the fuel gas.

(2) Treatment Period

[0096] It is preferable for the value of the flame treatment period (blow period) to be within a range of 0.1 to 100 seconds.

[0097] The reason for this is, that if the value of the flame treatment period is below 0.1 seconds, the modifying effect of the modifying compound does not appear evenly in some cases. On the other hand, if the value of the flame treatment period is above 100 seconds, the solid substrate subject to surface modifying will be heat deformed or heat damaged in some cases, and the types of solid substrates that may be used will be excessively limited in some cases.

[0098] Therefore, it is more preferable for the value of the flame treatment period to be within a range of 0.3 to 30 seconds, and it is even more preferable for the value of the flame treatment period to be within a range of 0.5 to 20 seconds.

[Second Embodiment]

[0099] The second embodiment is a surface modified solid substrate wherein the surface of the solid substrate is blow treated wholly or partly with a fuel gas flame with the respective boiling point being between 10 and 100 °C so that the wetting index has a value in a range from 40 to 80 dyn/cm (measuring temperature 25 °C).

1. Solid Substrate

(1) Rubber

[0100] According to the composition of the surface modified solid substrate, for the solid substrate at least one rubber type may be given selected from the group consisting of silicone rubber, fluorine-contained rubber, natural rubber, neoprene rubber, chloroprene rubber, urethane rubber, acryl rubber, olefin rubber, styrene-butadiene rubber, acrylonitrile-butadiene rubber, ethylene-propylene rubber, ethylene-propylenediene rubber, butadiene rubber, butyl rubber, styrene type thermoplastic elastomer and urethane type thermoplastic elastomer.

[0101] Among these rubber types an excellent modifying effect may be obtained according to the surface modification of the present invention with large wetting angle of contact, low wetting index silicone rubber, fluorine-contained rubber, olefin rubber, ethylene-propylene rubber. Therefore, it becomes easy to print numbers and letters and the like on the surface of stain-proof rubber and dirt covers such as silicone rubber, fluorine-contained rubber and the like.

(2) Resins

[0102] According to the composition of the surface modified solid substrate, the solid substrate may be given as at least one resin selected from the group consisting of a polyethylene resin (high density polyethylene, medium density polyethylene, low density polyethylene, high pressure polyethylene, medium pressure polyethylene, low pressure polyethylene, linear low density polyethylene, branch low density polyethylene, high pressure linear low density polyethylene, super molecular weight polyethylene, cross-linked polyethylene), polypropylene resin, denatured polypropylene resin, polymethyl pentene resin, polyester resin, polycarbonate resin, polyether sulfone resin, polyacryl resin, polyether ether ketone resin, polyimide resin, polysulfone resin, polystyrene resin, polyamide resin, and polyphenylen sulfide resin, ethylene-tetrafluoroethylen copolymer, polyvinyl fluoride resin, atetrafluoroethylene-perfluoroether copolymer, tetrafluoroethylene-hexafluoropropylene copolymer, polytetrafluoroethylene resin, polyvinylidene fluoride resin, polytrifluorochloroethylene resin and ethylene-trifluorochloroethylene copolymer.

[0103] Among these resin types an excellent modifying effect may be obtained according to the surface modification of the present invention with large wetting angle of contact, a low wetting index polyethylene resin, polypropylene resin, polyester resin, polycarbonate resin, polytetrafluoroethylene resin and the like.

[0104] Therefore, the printing of letters and patterns onto films made of a polyethylene resin or a polypropylene resin, or onto receptacles made of polyester, the firm adhering of aluminum reflecting film to compact disk boards made of a polycarbonate resin and also the printing of numbers and letters and the like onto dirt-repellent material made of a polytetrafluoroethylen resin become possible.

(3) Thermosetting Resins

[0105] According to the composition of the surface modified solid substrate, the solid substrate is at least one thermosetting resin selected from the group comprising of an epoxy resin, phenol resin, cyanate resin, urea resin, guanamine resin and the like. Among these thermosetting resins, in case of an epoxy resin for example, lasermarking on semiconductor plastic encapsulation resins may be carried out easily according to the surface modification of the present invention.

(4) Metals

[0106] According to the composition of the surface modified solid substrate, one or a combination of two or more from a group comprising aluminum, magnesium, stainless steel, nickel, chromium, tungsten, gold, copper, iron, silver, zinc, tin, lead and the like are preferable.

[0107] For example, aluminum is widely used as a light metal, but shows the problem of an easy surface oxidation layer forming, which leads to easy peeling-off (detachment) of UV curing paint and the like even when applied directly. Now, by carrying out silicatizing flame treatment and the like on the aluminum surface, the peeling-off (detachment) of UV curing paint and the like even when applied directly may be effectively prevented.

[0108] Further, magnesium as a recyclable metal is widely used in recent years in personal computer bodies and the like, but shows the problem of easy peeling-off (detachment) of UV curing paint and the like even when applied directly due to poor surface smoothness. Now, by carrying out silicatizing flame treatment and the like on the magnesium surface, the peeling-off (detachment) of UV curing paint and the like even when applied directly may be effectively prevented and colored magnesium sheets and the like may be provided.

[0109] Further, currently, when gold bumps or solder bumps of semiconductor elements are electrically connected to film carrier and circuit board in a high temperature and high moisture environment, problems appear with occurring

surface detachment Now, by carrying out silicatizing flame treatment and the like on either the gold bumps or solder bumps, or the film carrier or circuit board, the surface detachment may be effectively prevented.

[0110] Further, the silicatizing flame treatment and the like is a treatment using a flame which comprises a silicon atom, a titan atom or an aluminum atom, which enables the forming of a silicon oxide layer, titanium oxide layer or an aluminum oxide layer on the whole substrate substance or on part of it by blazing heat decomposition of the substrate substance.

(5) Inorganic Filler

[0111] As a solid substrate composing additive, it is also preferable to add one or a combination of two or more from a group comprising titanium oxide, zirconium oxide, indium oxide, tin oxide, silica, talc, calcium carbonate, lime, zeolite, gold, silver, copper, zinc, nickel, tin, lead, solder, glass, ceramic and the like.

[0112] By adding such an inorganic filler the physical properties such as the mechanical strength, the heat resistance, the electroconductivity or electrical insulation properties may be improved according to the type of inorganic filler. Not only that, by adding an inorganic filler in such a way, the surface of the inorganic filler itself will also be modified taking priority, so that as a result, the surface modifying effect develops even better than in case of a homogeneous solid substrate.

[0113] Further, when adding inorganic fillers into the solid substrate, it is preferable for the value of the added amount to be within a range of 0.01 to 80 weight% of the total amount of solid substrate, it is more preferable for the value to be within a range of 0.1 to 50 weight%, and it is even more preferable for the value to be within a range of 1 to 30 weight%.

(6) Form

[0114] The form of the solid substrate undergoing the treatment is not especially restricted, but for example can have a board shape, plate shape, sheet shape, film shape, tape shape, strip shape, panel shape, strap shape plane structure as well as a cylinder shape, column shape, sphere shape, block shape, tube shape, pipe shape, concavo-convex shape, membrane shape, fiber shape, fabrics shape, bundle shape three-dimensional structure.

[0115] For example, by carrying out silicatizing flame treatment and the like on fiber glass or carbon fiber, the surface may be modified and activated, and the fibers may be distributed evenly in a matrix resin such as epoxy resin and a polyester resin. Therefore, excellent mechanical strength, heat resistance and the like may be achieved in FRP and CFRP.

[0116] Further, as such a form of matter subject to treatment, it is also preferable for it to be of a composite structure such as of a solid substrate combined with a metal part, ceramic part, glass part, paper part, wooden part and the like.

[0117] For example, by carrying out silicatizing flame treatment on the inner side of a metal pipe or a ceramic pipe the surface is modified and activated and a layered pipe with an extremely strong resin liner may be obtained.

[0118] Further, by carrying out silicatizing flame treatment wholly or in part of the surface of a board, that is a plastic board or glass board, such as a liquid crystal display device, organic electro luminescence device, plasma display device, or a CRT and the like, an organic film such as a color filter, deflection sheet, light scattering sheet, black matrix sheet, anti-reflection film, anti-static film may be laminated extremely evenly and firmly.

2. Fuel Gas

[0119] As the same modifying compound and inflammable gas may be used as described in the first embodiment, the description is omitted here.

3. Flame

[0120] As the same flame temperature and treatment period may be used as described in the first embodiment, the description is omitted here.

4. Wetting Index (Surface Energy or Surface Tension)

(1) After Surface Modification

[0121] Further, it is preferable for the value of the wetting index of the surface modified solid substrate to be in a range between 40 and 80 dyn/cm (measuring temperature 25 °C).

[0122] The reason for this is, that if the value of the wetting index of the solid substrate is below 40 dyn/cm, easy adhesion, printing, painting and the like becomes difficult in some cases. On the other hand, if the value of the wetting

index of the solid substrate is above 80 dyn/cm, the surface treatment is overly carried out and the solid substrate is heat damaged in some cases.

[0123] Therefore, it is more preferable for the value of the wetting index of the surface modified solid substrate to be in a range between 45 and 75 dyn/cm, and it is even more preferable for the value to be in a range between 50 and 70 dyn/cm.

(2) Before Surface Modification

[0124] Further, it is preferable for the value of the wetting index of the solid substrate before surface modification (before surface treatment) to be in a range between 20 and 45 dyn/cm (measuring temperature 25 °C).

[0125] The reason for this is, that if the value of the wetting index of the solid substrate is below 20 dyn/cm, the surface treatment needs to be carried out over a long period, so that the solid substrate is heat damaged in some cases. On the other hand, if the value of the wetting index of the solid substrate is above 45 dyn/cm, efficient surface treatment by flame becomes difficult in some cases. For example, the wetting index of polyethylene resin before modification treatment is about 40 dyn/cm, and although it also depends on the silicatizing flame treatment temperature and the like, with about 1 second of silicatizing flame treatment the wetting index may be increased to about 60 dyn/cm.

[0126] Therefore, it is more preferable for the value of the wetting index of the solid substrate before surface modification (before surface treatment) to be in a range between 25 and 38 dyn/cm (measuring temperature 25 °C), and it is even more preferable for the value to be in a range between 28 and 36 dyn/cm.

5. Contact Angle

(1) After Surface Modification

[0127] Further, it is preferable for the value of the contact angle of the surface modified solid substrate, measured using water, to be in a range between 0.1 and 30 degrees (measuring temperature 25 °C).

[0128] The reason for this is, that if the value of the contact angle of the solid substrate is below 0.1 degree, the surface treatment is overly carried out, so that the solid substrate is heat damaged in some cases. On the other hand, if the value of the contact angle of the solid substrate is above 30 degrees, easy adhesion, printing, painting and the like becomes difficult in some cases.

[0129] Therefore, it is more preferable for the value of the contact angle of the surface modified solid substrate, measured using water, to be in a range between 0.5 and 20 degrees (measuring temperature 25 °C), and it is even more preferable for the value to be in a range between 1 and 10 degrees.

[0130] Table 1 shows the wetting index (dyn/cm) of the solid substrate before surface treatment and a measurement example of the wetting index of the solid substrate after surface treatment (for 0.5 seconds) measured using a standard (reference) liquid at 25 °C.

(2) Before Surface Modification

[0131] Further, it is preferable for the value of the contact angle, measured using water, of the solid substrate before surface modification (before surface treatment) to be in a range between 50 and 120 degrees (measuring temperature 25 °C).

[0132] The reason for this is, that if the value of the contact angle of the solid substrate is below 50 degrees, efficient surface treatment by flame becomes difficult in some cases. On the other hand, if the value of the contact angle of the solid substrate is above 120 degrees, the surface treatment needs to be carried out over a long period of time, so that the solid substrate is heat damaged in some cases. For example, the contact angle of polytetrafluoroethylene resin before modification treatment is about 108 degrees, and although it also depends on the silicatizing flame treatment temperature and the like, with about 1 second of silicatizing flame treatment the contact angle may be decreased to about below 20 degrees.

[0133] Therefore, it is more preferable for the value of the contact angle of the solid substrate before surface modification (before surface treatment), measured using water, to be in a range between 60 and 110 degrees, and it is even more preferable for the value to be in a range between 80 and 100 degrees.

[Third Embodiment]

[0134] The third embodiment is an apparatus 10 for modifying a surface of a solid substrate, as shown in Figure 1, containing a storage tank 12 for storing a modifying compound 14 which comprises a silicon atom, a titan atom or an aluminum atom, with the respective boiling point being between 10 and 100 °C, a transfer part 24 for transferring the

fuel gas and an outlet part 32 for letting out the fuel gas flame 34 for blow treatment

1. Storage Tank

[0135] It is preferable for there to be a first storage tank 12, as shown in Figure 1, for storing the modifying compound 14, having a heating means 16, and a second storage tank (not shown) for storing an inflammable gas such as compressed air. In this example, a heating means 16 is included in the bottom part of the first storage tank 12, the heating means 16 being composed of a heater and heat transfer line, or a heating board or the like that is connected to a heat exchanger, for evaporating the modifying compound 14 being liquid at ambient temperature and atmospheric pressure.

[0136] When the solid substrate is surface treated, it is preferable for the modifying compound 14 inside the first storage tank 12 to be heated by the heating means 16 to a predetermined temperature, and in evaporated state to be mixed with the inflammable gas (air etc.) to form the fuel gas.

[0137] Furthermore, because the amount of modifying compound included in the fuel gas is of extreme importance, the amount of this modifying compound should also be indirectly controlled. It is therefore preferable to monitor the modifying compound's steam pressure (or the modifying compound amount) by providing a pressure gauge (or a liquid surface level gauge) 18 in the first storage tank 12.

2. Transfer Part

[0138] The transfer part is usually a pipe structure, and as shown in Figure 1, preferably contains a mixing chamber 22 for forming the fuel gas by evenly mixing the modifying compound 14 transferred from the first storage tank 12 and the inflammable gas (air) transferred from the second storage tank (not shown), as well as a valve and throughput gauge to control the throughput, or a pressure gauge 28 to control the fuel gas pressure.

[0139] Further to mixing the modifying compound and inflammable gas evenly, a mixing pump in the mixing chamber 22 in order to strictly control the throughput and an obstruction board or the like to prolong the retention period are preferably included.

3. Outlet Part

(1) Structure

[0140] The outlet part, as shown in Figure 1, preferably comprises a burner 32 for blow treatment of the solid substrate subjected to treatment with a flame 34 obtained by burning the fuel gas transferred from the transfer part 24. The type of bumer is not particularly restricted, for example, a premixing type burner, a diffusion type burner, a partial-premixing type burner, a spraying burner, an evaporation burner, a pulverized coal burner and the like. Further, the form of bumer is not particularly restricted, for example, as shown in Figure 1, the form may be a fan-type as a whole spreading toward the tip portion, or as shown in Figure 4, the form of the burner may be a rectangle with jet nozzles 64 being aligned along the sides.

(2) Arrangement

[0141] It is preferable to determine the arrangement of the outlet part, that is to say, the layout of the burner taking into consideration the ease of surface modification of the solid substrate subject to treatment.

[0142] For example, it is preferable to arrange it along a circular or elliptical shape as shown in Figure 2, but it is also preferable to arrange it adjacent to both sides of a solid substrate subject to treatment as shown in Figure 4.

[0143] Further, it is also preferable to arrange it at a prescribed distance from one of the sides of a solid substrate subject to treatment as shown in Figure 5 a, but it is also preferable to arrange it at a prescribed distance each from both sides of a solid substrate subject to treatment as shown in Figure 5 b.

4. Form

(1) Stationary Type

[0144] The apparatus for modifying a surface of a solid substrate preferably comprises, for example, as shown in Figure 1, a storing tank 12, a transfer part 24 for transferring the fuel gas, and an outlet part 32 for blow treatment with a flame obtained from the fuel gas, and the respective parts are installed. As shown in Figure 2, the solid substrate, mounted on a fixing jig 38 on a rotation table 36, is preferably blow treated with a flame 34 from the outlet part 32 with changing its position of the solid substrate subject to treatment and rotating the solid substrate by the fixing jig 38.

[0145] According to the stationary type of apparatus 10 for modifying the surface of the solid substrate, the surface of the solid substrate subject to treatment may be modified in large scale and efficiency.

(2) Portable Type

[0146] The apparatus for modifying a surface of a solid substrate 42 is preferably a portable type as shown in Figure 3. That is to say, as shown in the region surrounded by the dotted lines, the apparatus comprises a cartridge-type storing tank 46, a laying pipe 47, a box 44 provided with a throughput gauge and a pressure gauge, wherein the laying pipe 47 comprises a burner 32 in its tip portion. According to the above construction, by transferring the box 44 timely, both the solid substance subject to treatment being placed outdoors and the solid substance subject to treatment having a large size and capacity may be surface modified easily.
In order to carry the box easily, the box 44 is preferably provided with a handle or a cord on its upper portion, and the weight of the box 44 is preferably 20 kg or less.

[Example 1]

1. Surface Modification of a Solid Substrate

[0147] On a 2mm strong silicone rubber sheet (hardness 80) silicatizing flame treatment was carried out for 0.5 seconds using a portable surface modifying apparatus as shown in Figure 3.
[0148] Furthermore, as a fuel gas a mixed gas cartridge was used with 0.0001 mol% of tetramethyl silane having a boiling point at 27 °C, 0.00001 mol% of tetramethoxyl silane having a boiling point at 122 °C and the remainder being compressed air.

2. Evaluation of the Solid Substate

(1) Wetting Index (Surface Tension)

[0149] The wetting index of a surface modified silicone rubber sheet was measured using a standard liquid. Further, the wetting index of the silicone sheet before surface modification was measured in the same way.

(2) UV Paint Properties

[0150] After screen printing an epoxy-acrylate type UV curing paint onto a surface modified silicone rubber sheet, 300 mJ/cm^2 of UV rays were irradiated with an UV irradiation apparatus and it was evaluated according to the standard as stated below.
[0151] Further, the UV paint properties of the silicone sheet before surface modification were measured in the same way.

very good:	According to the cross cut adhesion test of 100 pieces (JIS Standard), no piece was peeled off.
good:	According to the cross cut adhesion test of 100 pieces (JIS Standard), 1 or 2 piece(s) was(were) peeled off.
fair:	According to the cross cut adhesion test of 100 pieces (JIS Standard), 3 to 10 pieces were peeled off.
bad:	According to the cross cut adhesion test of 100 pieces (JIS Standard), more than 11 pieces were peeled off.

[Examples 2 - 7]

[0152] In Examples 2 - 7, as shown in Table 1, the type of solid substrate subject to treatment and the silicatizing flame treatment period were changed, and the surface modified solid substrate was evaluated in the same way as Example 1.

[Comparison Example 1]

[0153] Instead of the mixed gas of compressed air with tetramethylsilane and tetramethoxysilane of Example 1, a mixed gas of compressed air with tetramethoxysilane alone with a boiling point of 122 °C was used, but apart from that, the solid substrate was surface modified and evaluated in the same way as in Example 1.

Table 1

	Solid Substrate	Modifying treatment time (sec.)	Wetting index (dyn/cm)		UV Painting	
			Before Treatment	After Treatment	Before treatment	After treatment
Example 1	Silicone Rubber	0.5	30	60	bad	very good
Example 2	Silicone Rubber	0.2	30	52	bad	good
Example 3	Polyethylene Board	1.0	32	64	bad	very good
Example 4	Polyethylene Film	0.2	38	64	fair	very good
Example 5	Magnesium Board	0.5	34	60	bad	very good
Example 6	Stainless Steel Board	0.5	34	60	bad	very good
Example 7	Aluminum Board	0.5	32	60	bad	very good
Comparison Example 1	Silicone Rubber	0.5	30	48	bad	fair

[Examples 8 - 9 and Comparison Example 2]

[0154] In Example 8, after carrying out silicatizing flame treatment in the same way as in Example 1, the shelf period (rest period) was changed to 2 weeks and to 4 weeks, and the wetting index and the UV paint properties were each evaluated.

[0155] Further, in Example 9, instead of the mixed gas of compressed air with tetramethylsilane and tetramethoxysilane of Example 1, a mixed gas of compressed air with tetramethylsilane was used, and apart from that, after carrying out silicatizing flame treatment in the same way as in Example 1, the rest period was changed to 2 weeks and to 4 weeks, and the wetting index and the UV paint properties were each evaluated.

[0156] Further, in Comparison Example 2, instead of silicatizing flame treatment, corona treatment was carried out, and the wetting index and the UV paint properties were each evaluated. Obtained results are shown in Table 2.

Table 2

	Solid Substrate	Modifying Treatment (time)	Wetting Index (dyn/cm)		UV Painting	
			2weeks	4weeks	2weeks	4weeks
Example 8	Silicone Rubber	silicatizing flame A 0.5 sec.	60	60	very good	very good
Example 9	Silicone Rubber	silicatizing flame B 0.5 sec.	60	60	very good	very good
Comparison Example 2	Silicone Rubber	Coronatreatment 10 sec.	30	30	bad	bad

* silicatizing flameA (tetramethylsilane and tetramethoxysilane)
* silicatizing ftameB (tetramethylsilane)

Industrial applicability

[0157] As the above description explains, according to the method for a modifying a surface of a solid substrate in connection with the present invention, by blow treating a solid substrate with a flame of a fuel gas which comprises a modifying compound, with the respective boiling point being between 10 and 100 °C, a surface modified solid substrate may be obtained with facilitated adhesion, printing, painting and the like.

[0158] Further, even if the surface modified solid substrate of the present invention is for example a representative of a difficult adhesion material like silicone rubber or fluorine-contained rubber, olefin resin or polyester resin, or a metal such as stainless steel or magnesium, adhesion, printing and painting, that had been impossible up to now, has become easily possible. Consequently, adhesion, printing and painting have easily become possible onto surfaces of a dirt-repellent rubber, a water-repellent rubber, a cushion rubber, a sealing rubber and the like as a matter of course, and also onto products out of these materials with difficult adhesion such as all kinds of switches, covers, levers, vehicle bumpers, electric appliance bodies, electronic part bodies, containers, films, tapes and the like.

[0159] Furthermore, according to the apparatus for modifying a surface of a solid substrate in connection with present invention, by including a storage tank for storing a specific fuel gas, a transfer part for transferring said fuel gas to an outlet part, and an outlet part for blow treating with a fuel gas flame, allows to efficiently obtain a solid substrate facilitating adhesion, printing and painting.

Claims

1. A method for modifying a surface of a solid substrate, wherein the surface of the solid substrate is treated wholly or partly with a flame of a fuel gas which comprises a modifying compound which comprises a silicon atom, titan atom or aluminum atom, with the respective boiling point being between 10 and 100 °C.

2. The method for modifying a surface of a solid substrate as recited in claim 1, wherein the modifying compound is at least one compound selected from the group consisting of an alkylsilane compound, alkoxysilane compound, alkyltitanium compound, alkoxytitanium compound, alkylaluminum compound and alkoxyaluminum compound.

3. The method for modifying a surface of a solid substrate as recited in claim 1 or 2, wherein at least one compound with a boiling point of 100 °C or above selected from the group consisting of an alkylsilane compound, alkoxysilane compound, alkyltitanium compound, alkoxytitanium compound, alkylaluminum compound and alkoxyaluminum compound is added to the modifying compound, the added amount having a value in a range from 0.01 to 50 mol% of the total amount of modifying compound.

4. The method for modifying a surface of a solid substrate as recited in anyone of claims 1 - 3, wherein the amount of the modifying compound in the fuel gas has a value in a range from 1×10^{-10} to 10 mol% of the total amount of fuel gas.

5. The method for modifying a surface of a solid substrate as recited in anyone of claims 1 - 4, wherein the modifying compound is heated, evaporated and then burned.

6. The method for modifying a surface of a solid substrate as recited in anyone of claims 1 - 5, wherein the fuel gas is obtained by mixing the modifying compound into an air stream.

7. The method for modifying a surface of a solid substrate as recited in claim 6, wherein the modifying compound is mixed into the air stream via a carrier gas.

8. The method for modifying a surface of a solid substrate as recited in anyone of claims 1 - 7, wherein the surface of a solid substrate is treated with the flame while the pressure change of the fuel gas is continuously or intermittently monitored.

9. The method for modifying a surface of a solid substrate as recited in anyone of claims 1 - 8, wherein the wetting index has a value in a range from 40 to 80 dyn/cm (measuring temperature 25 °C)

10. The method for modifying a surface of a solid substrate as recited in anyone of claims 1 - 9, wherein the flame temperature has a value in a range from 500 to 1500 °C.

11. The method for modifying a surface of a solid substrate as recited in anyone of claims 1 - 10, wherein the flame treatment period has a value in a range from 0.1 to 100 seconds.

12. A surface modified solid substrate, wherein the surface of the solid substrate is treated wholly or partly with a fuel gas flame so that the wetting index has a value in a range from 40 to 80 dyn/cm (measuring temperature 25 °C), the fuel gas of the flame comprising a modifying compound which comprises a silicon atom, a titanium atom or an aluminum atom, with the respective boiling point being between 10 and 100 °C.

13. The surface modified solid substrate as recited in claim 12, wherein the wetting index of the solid substrate before the surface treatment has a value in a range from 20 to 45 dyn/cm (measuring temperature 25 °C).

14. The surface modified solid substrate as recited in claim 12 or 13, wherein the solid substrate is at least one inorganic substance selected from the group consisting of aluminum, magnesium, stainless steel, titanium oxide, zinc oxide and zirconium oxide.

15. The surface modified solid substrate as recited in claim 12 or 13, wherein the solid substrate is at least one rubber selected from the group consisting of silicone rubber, fluorine-contained rubber, natural rubber, neoprene rubber, chloroprene rubber, urethane rubber, acryl rubber, olefin rubber, styrene-butadiene rubber, acrylonitrile-butadiene rubber, ethylene-propylene rubber, ethylene-propylenediene rubber, butadiene rubber, butyl rubber, styrene type thermoplastic elastomer and urethane type thermoplastic elastomer.

16. The surface modified solid substrate as recited in claim 12 or 13, wherein the solid substrate is at least one resin selected from the group consisting of a polyethylene resin, polypropylene resin, polymethyl pentene resin, polyester resin, polycarbonate resin, polyether sulfone resin, polyacryl resin, polyether ether ketone resin, polyimide resin, polysulfone resin, polystyrene resin, polyamide resin, and polyphenylen sulfide resin, ethylene-tetrafluoroethylen copolymer, polyvinyl fluoride resin, tetrafluoroethylene-perfluoroether copolymer, tetrafluoroethylene-hexafluoropropylene copolymer, polytetrafluoroethylene resin, polyvinylidene fluoride resin, polytrifluorochloroethylene resin and ethylene-trifluorochloroethylene copolymer.

17. The surface modified solid substrate as recited in claim 12 or 13, wherein the solid substrate is at least one thermosetting resin selected from the group consisting of an epoxy resin, phenol resin, cyanate resin, urea resin, and guanamine resin.

18. An apparatus for modifying a surface of a solid substrate, comprising: a storage part for storing the fuel gas which comprises a modifying compound which comprises a silicon atom, a titanium atom or an aluminum atom, with the respective boiling point being between 10 and 100 °C; a transfer part for transferring the fuel gas to an outlet part; and an outlet part for letting out the fuel gas flame for blow treatment.

19. The apparatus for modifying a surface of a solid substrate as recited in claim 18, comprising a heating means in the storage part for producing the fuel gas by evaporating the modifying compound.

Fig. 1

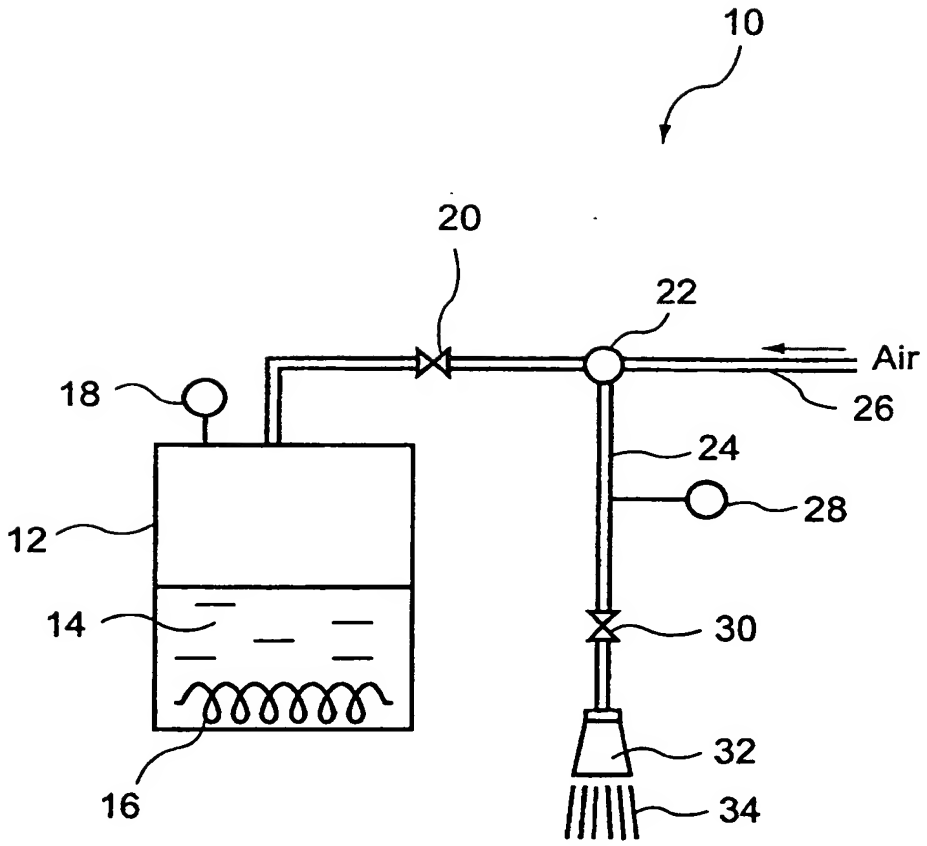


Fig. 2

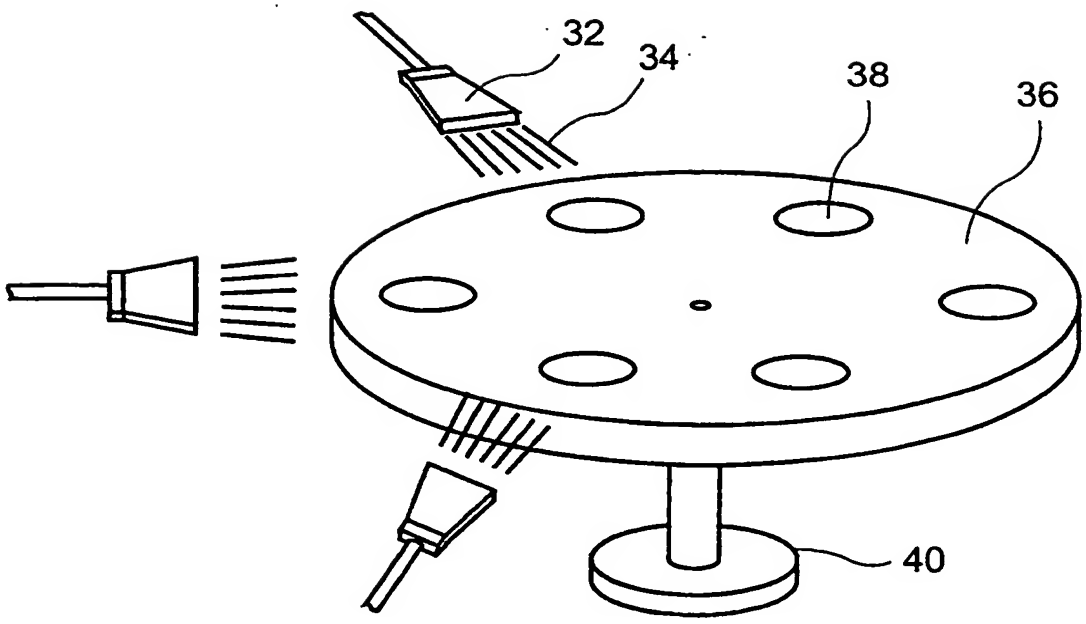


Fig. 3

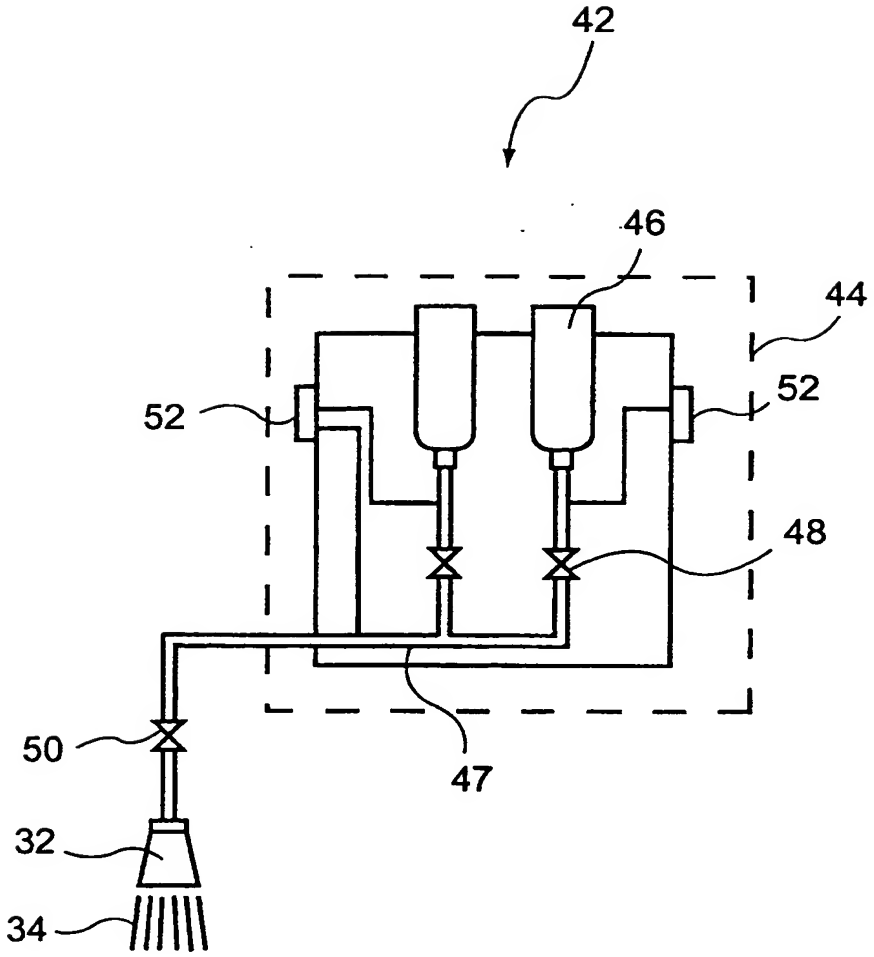


Fig. 4

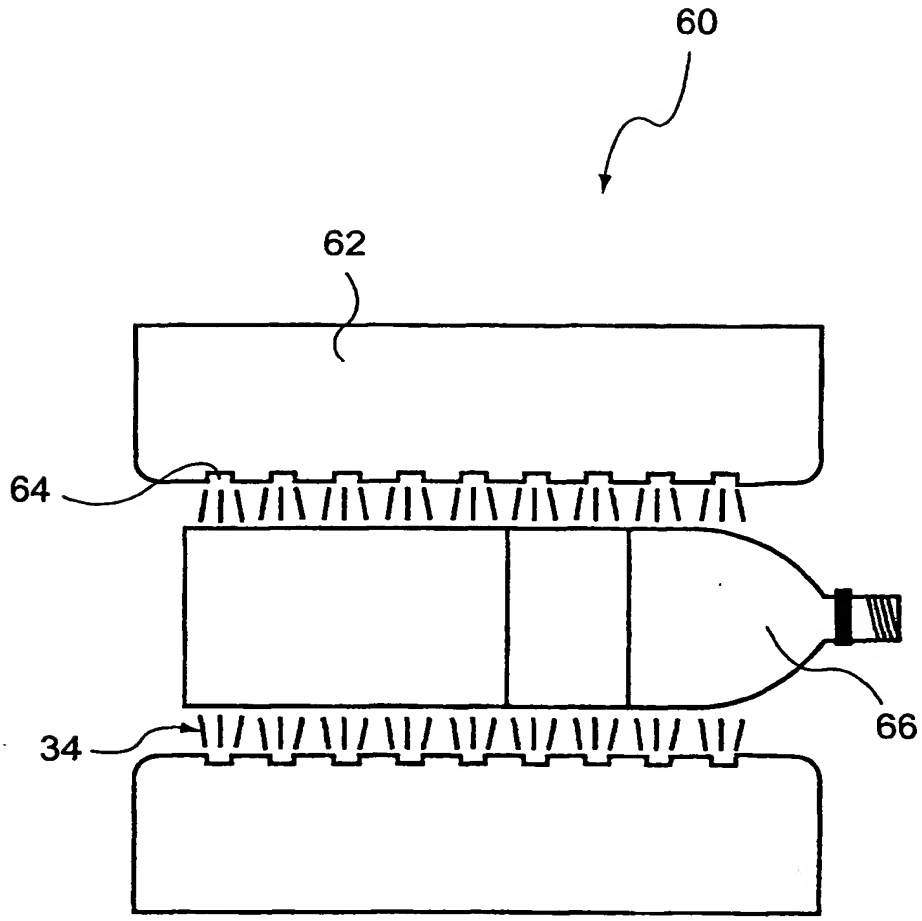
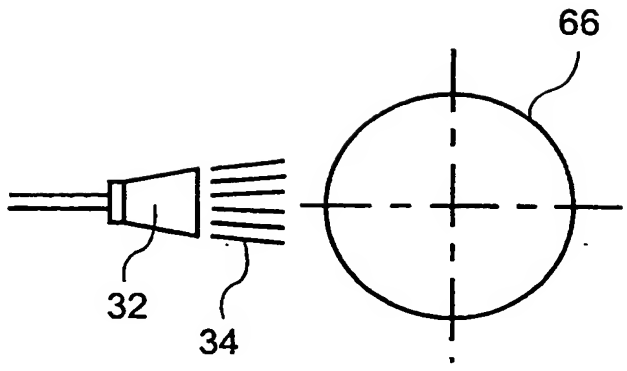
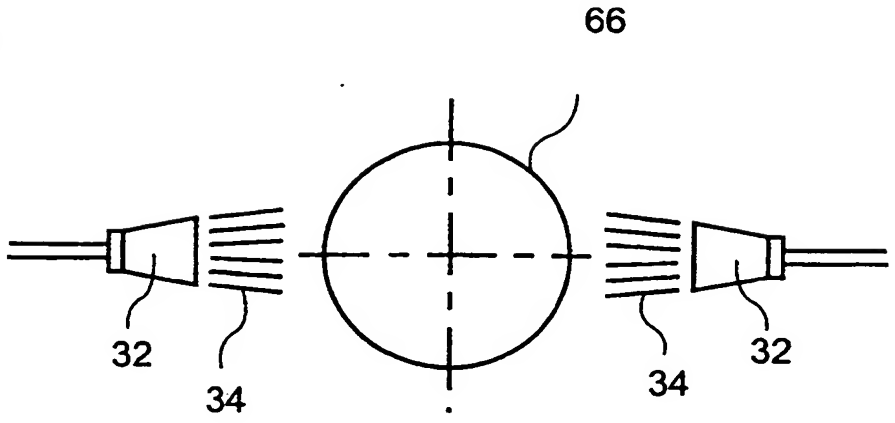


Fig. 5

(a)



(b)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP03/01356

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C23C16/00, C08J7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] C23C16/00-16/56, C23C24/00-30/00, B29C59/08,
B32B1/00-35/00, C08J7/00-7/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Jitsuyo Shinan Toroku Koho	1996-2003
Kokai Jitsuyo Shinan Koho	1971-2003	Toroku Jitsuyo Shinan Koho	1994-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTP FILE(JOIS)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 2000-272249 A (Teijin Ltd.), 03 October, 2000 (03.10.00), Claims; Par. No. [0022] (Family: none)	12-17 1-11,18,19
A	EP 594171 A1 (FLACHGLAS AG.), 27 April, 1994 (27.04.94), Full text & DE 4237921 A1 & CZ 9302226 A3	1-19
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☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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21 April, 2003 (21.04.03)	06 May, 2003 (06.05.03)
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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